AQUANAUTICS CORPORATION
TECHNICAL REPORT -OXYGEN CHEMISTRY

ARPA ORDER NO:	4696
CONTRACT NO:	N00014-87-C-0334
EFFECTIVE DATE OF CONTRACT:	1/1/87
EXPIRATION DATE OF CONTRACT:	10/31/87
PRINCIPAL INVESTIGATOR:	N. ROSS BUCKENHAM
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REPORTING PERIOD:	January 1, 1987 through August 31, 1987

* REPORT SUMMARY / TECHNICAL PROBLEM / GENERAL METHODOLOGY / TECHNICAL RESULTS

See attached report

* IMPLICATIONS FOR FURTHER RESEARCH

As described in proposal Number:093087-1,200 titled, "Additional Scope of Work and Funding Request to Supplement and Extend DARPA Contract No.: N00014-87-C-0334", Dated: September 30, 1987

* SPECIAL COMMENTS

None

QUARTERLY REVIEW: Engineering, July - September '87

PROJECT: DARPA

WRITTEN BY: Sam Mohanta

DATE: October 16, 1987

PROJECT OBJECTIVE: To demonstrate the technology of oxygen extraction from seawater by designing a submarine powered by a fuel cell and oxygen supplied by Aquanautics system.

STATUS AT THE END OF PREVIOUS QUARTER:

PROGRESS DURING THIS QUARTER:

A. Project Management: A review meeting was held with personnel from DARPA, NOSC, ARION, MDS and Makai. In this meeting, progress during last quarter was reviewed and project scope for the year 1988 was addressed. A new PERT-CPM chart has been produced to reflect the revised scope of work.

B. Electrochemical Cell:

i) Cell Design: A new cell design concept has been introduced where the carrier fluid flows through the felt in a direction perpendicular to membrane separator. This allows much lower pressure head and therefore lowers pumping costs since the fluid velocity and path length are small. The fluid also passes through all the electric potentials of the electrodes.

ii) Cell Improvements: A few opportunities for reductions in the energy requirements in the cell improvements have also been identified. These are:

1) use of higher conductivity solution
2) better contact between current collector and electrode material.
3) possible use of microporous separators

All these improvements are particularly beneficial at higher current density operation. The direct resistive loss in the cell at 10mA/cm^2 is about 40 mV and constitutes an energy consumption of 10w/lpm of oxygen. Higher conductivity of electrolyte will also reduce the potential variation through the electrode bed depth. This in turn will lead to more uniform current distribution through the bed depth, with higher yield of oxygen per unit volume.

iii) Cell Scale-up: Two larger sizes of cell have been tested to check whether the laboratory cell (2.5 x 10 cm^2) performance scales up. The cell sizes tested were 10 x 10 cm^2 and 15 x 28 cm^2. While the former did show scaled up performance values, the performance of the latter was not as good. The failure to scale can be attributed to channeling of carrier fluid around the edges of the electrode and the longer path length through which fluid has to travel in the electrode. See figure for performance of various cell sizes.

C Pumping Power: Pumping power required plays an important role in the design of the present vehicle. In this quarter, pressure heads at various flow rates were measured for felt, laboratory cells, and commercially available cells.

A model describing the operating conditions of the electrochemical cell necessary to meet electrochemical and pumping energy requirements has been devised.

PLAN FOR THE QUARTER OCTOBER - DECEMBER, 1987:

The following activities are planned to be carried out this quarter.

1) Scale Up of Cell Performance: The objective is to scale up the best performance obtained in laboratory cells to the large, demonstration scale cells.

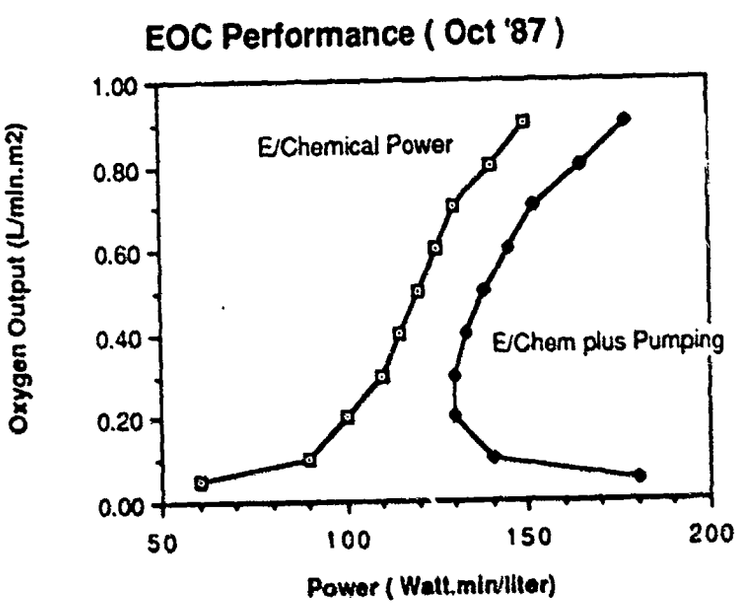
2) Alternate Cell Design: A small flow through cell will be designed and it's performance compared with standard flow by cell.

3) Fuel Cell: Eltech personnel will install a 3-cell stack and train personnel at Aquanautics to operate the system. The cell stack will then be tested.

4) Integration: A small-scale integration of fuel cell - EOC system (oxygen generated by EOC will be directly fed into the fuel cell) will also be attempted.

5) Pump/Motor Research: High efficiency pump and motor are very desirable for this application. Research will be carried out to find the most efficient, commercially available pump and motor which are suitable for our use.

6) Air-loader Preliminary Experiment: Air-loader will be used in the preliminary runs of the system. Some experiments will be carried out to determine the operating parameters for the full scale system.



PERFORMANCE RESULTS FOR CELL SCALE-UP EXPERIMENTS,
SWEEP GAS N_2 AND CELL VOLTAGE 0.7 V

CELL	# CELLS	CELL SIZE CM x CM	CARRIER FLOW $ml/min/cm^2$	I mA/cm^2	ECO_2 $ml/min/cm^2$	POWER watt.min/ liter	EXP. CODE
EOC	1	2.5 x 10	1.8	6	0.032	120	4KK98B,8JV50-2, 3VLC2A
MP	10	10 x 10	2	5.8	0.042	98	3CB05b
SU	1	15 x 28	1.5	3.3	0.020	111	3CB24C

QUARTERLY REPORT

DARPA SCIENCE

JULY 21 - SEPTEMBER 30, 1987

Overall Goals and Objectives for Oxygen Extractor Technology

1. Minimize power requirements.

2. Maximize current density.

3. Determine lifetime of carriers.

Highlights of Progress Towards Goals

1) a) Confirmed mechanism of oxygen release for Cobalt 33 SP carrier. This allows the design of catalytic routes to reduce overall power.

b) From a) the structural factors necessary in mediators for successful catalysis of oxygen release were determined.

c) The mediators conforming to the design criteria generated by a) and b) were introduced into the analytic EOC units and the DU-apparatus. For the latter apparatus 10 mL/min of oxygen was produced at 22 $WminL^{-1}$ and 40ml/min of oxygen was produced at $100WminL^{-1}$ using an unoptimized solution.

2) a) The mechanism of oxygen release from Cobalt 33SP involves two steps at low potential. The first involves a chemical dissociation of the oxygenated complex and the second is the oxidation of the Cobalt (II) released by the dissociation step. The second step is catalysed by mediators and it is the mediators which carry the electrons to the electrode. Studies have been carried out to determine the best mediator/electrode material combination. The fastest electron transfer rates have been observed with platinum and TMDAB (see attached report on electrochemistry). The conclusions are that the electron transfer rates are sufficiently fast to justify a planar electrode design for the EOC. This is an important result since the cell engineering could be simplified by removal of the graphite felt electrodes.

b) The results of cyclic voltammetry experiments on mediators with 33 SP and Cobalt bishistidine indicate that the chemical step described in 2 a) may be the limiting step. Preliminary indications are that the rates of oxygen release are much faster for histidine than 33SP when the oxidation is catalyzed.

c) Analysis of the EOC current-voltage data indicates that even with 33SP the cathodic reaction may be rate-limiting when mediators are used. A study of the best materials for the cathode is now underway.

3) a) Considerable support work has been performed to help the engineering department with problems concerning the current collectors, rejuvenation and compression of felt electrodes. These properties all affect the current density. An EOC experiment has been carried out which gave 1 ml/min. at $100WminL^{-1}$ for over 50 hours. This is an acceptable lifetime for the demonstration.

b) An apparatus has been constructed which is designed to accelerate the electrochemical cycling process in the EOC. This involved a closed loop with no loader or unloader. For reasons which are unclear the Cobalt 33SP complex oxidized rapidly and irreversibly in the system. The rate constant of this reaction has been measured to be $2x10^{-4}s^{-1}$. At present it is not understood why this reaction is slowed down so much in the EOC but a new long-term apparatus will be constructed which incorporates a loader and an unloader.

c) The procedure for determining the K_{ML} and K_{O2} of the carrier compounds has been worked out and the results are shown in Table 3-1 of the attached report.

d) Experiments on degradation of 33SuzyP ligand shows that it reacts with oxygen. Chromatography conditions have been determined to allow analysis and possibly recycling of the carrier complex.

Theoretical Foundations

Except for the degradation problem an excellent qualitative understanding of the chemistry involved in the oxygen extractor technology has now been achieved. The initial work on developing quantitative models for the electrochemical kinetics has now been carried out and steps have been taken to obtain outside help with this theory through the Liquid Air partnership. The theory and initial experimental results show that carrier structure affects the electrochemical kinetics considerably.

Implications for Further Research

1) Initial results with the use of mediators with Co 33SP give a good level of confidence that this carrier can be used in the scale-up of the technology to the demonstration stage. A 25 kg. batch of 33SP has been ordered to allow this work to proceed. Optimization of the conditions is underway.

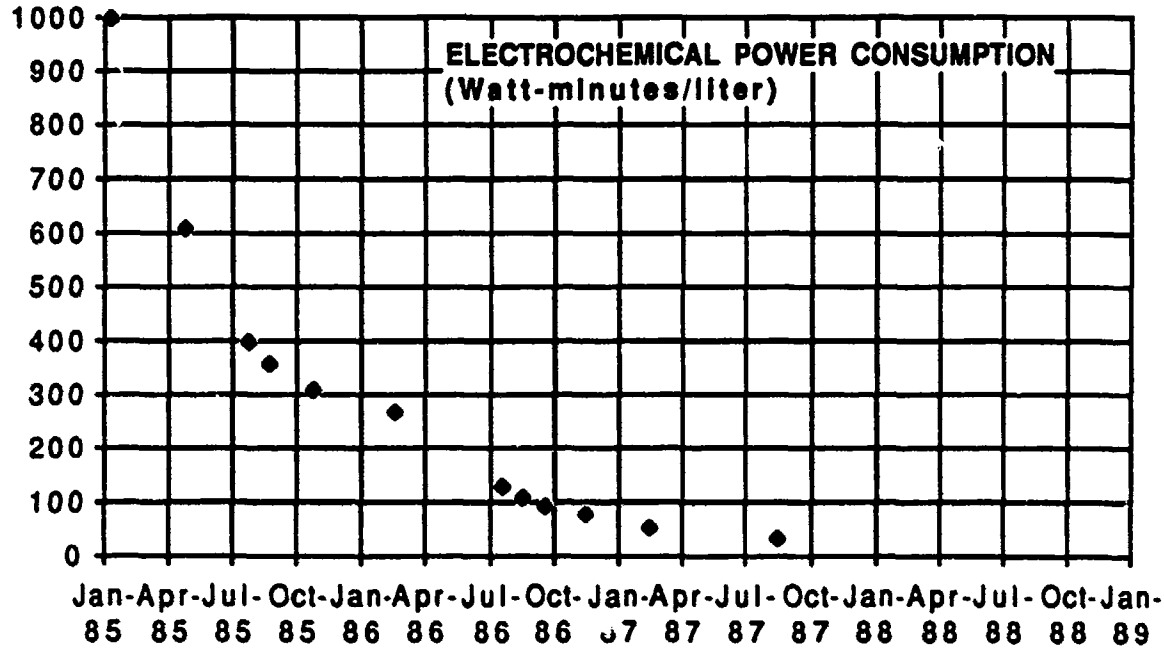
2) The degradation problems with Co 33SP are not so serious that the demonstration cannot be achieved but raise concerns for the technology beyond the demonstration stage. For this reason then it is necessary to perform work on a back-up carrier and to find one which is more stable.

3) Initial results show that although 33SP is thermodynamically an excellent carrier the kinetics have been observed to be sluggish. For this reason also new carriers need to be studied.

4) The success of the mediators in accelerating the anode indicates that the cathodic reaction may now be rate-limiting. More intensive studies on this reaction are necessary and once again a factor to be worked at here is the structure of the carrier thus implying more work on alternatives to 33SP.

Best Reproducible Data this Month

• Minimum EOC power with at least 0.15ml/minute of electrochemical oxygen	=	35 watt-min/liter with SP33 and TMDAB
• Best EOC oxygen output at 60-80 watts min/liter	=	1 ml/minute
• Best EOC longevity data	=	50 hrs. @ 1 ml/min and 100 w min/liter


ELECTROCHEMICAL POWER CONSUMPTION
(Watt-minutes/liter)
1000
900
800
700
600
500
400
300
200
100
0
Jan-85
Apr-85
Jul-85
Oct-85
Jan-86
Apr-86
Jul-86
Oct-86
Jan-87
Apr-87
Jul-87
Oct-87
Jan-88
Apr-88
Jul-88
Oct-88
Jan-89